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- [54] **METHOD FOR CONTACTING SOLIDS-CONTAINING FEEDS IN A LAYERED BED REACTOR**
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- [21] Appl. No.: 572,483
- [22] Filed: Jan. 20, 1984

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 547,162, Oct. 31, 1983, abandoned, which is a continuation of Ser. No. 316,387, Oct. 29, 1981, abandoned.
- [51] Int. Cl. B01J 8/02; C07C 3/34
- [52] U.S. Cl. 208/146; 422/217; 422/191
- [58] Field of Search 208/146, 147, 155, 156; 210/283, 290, 807; 422/191, 217

References Cited

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2,534,907	12/1950	Ham et al.	210/290
2,789,695	4/1957	Winkler et al.	210/807
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3,148,962	9/1964	Dellinger et al.	210/290
3,562,800	2/1971	Carlson et al.	208/216
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"Entrained Particle Collection in Packed Beds",

Stephen Jackson and Seymour Calvert, A.I.Ch.E. Journal, vol. 12, No. 6, pp. 1075-1078 (1966).

"Filtration of Aqueous Latex Suspensions Through Beds of Glass Spheres", Joseph A. Fitzpatrick & Lloyd A. Spielman, Journal of Colloid and Interface Science, vol. 43, No. 2, May 1973.

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ABSTRACT

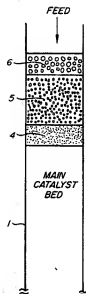
A packed bed reactor for hydrocarbon processing and method of use is provided. The reactor comprises:

(a) a first packed bed of particles in fluid communication with a feed inlet to said reactor, said first packed bed extending more than 3 to 18 inches in the direction of flow and comprising predominantly particles at least about $\frac{1}{8}$ inch in diameter;

(b) a second packed bed of particles in fluid communication with said first packed bed and downstream of said first packed bed, said second packed bed extending at least 12 to 48 inches in the direction of flow and comprising predominantly particles having diameters within the range of $\frac{3}{16}$ to $\frac{5}{16}$ inch and smaller than the average diameter of particles in said first bed; and

(c) a third packed bed of particles in fluid communication with said second packed bed and downstream of said second packed bed, said third packed bed comprising predominantly particles having diameters below $\frac{1}{8}$ inch.

14 Claims, 2 Drawing Figures



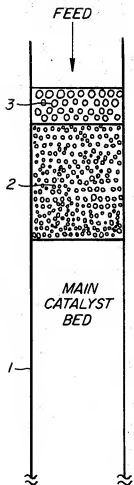


FIG. 1.

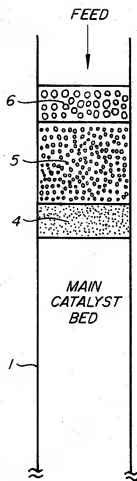


FIG. 2.

METHOD FOR CONTACTING SOLIDS-CONTAINING FEEDS IN A LAYERED BED REACTOR

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 547,162, filed Oct. 31, 1983, which in turn is a continuation of application Ser. No. 316,387, filed Oct. 26, 1981 both abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the chemical processing of hydrocarbonaceous fluid feeds containing suspended solids and more particularly to processing hydrocarbonaceous feedstocks under hydrocarbon conversion conditions in packed bed reactors. Packed bed reactors are employed in a number of industries for converting fluid feedstocks. The packing can be reactive material, catalytic material, or inert material and can also act as deposition sites for reactants or products.

Plugging problems can occur when packed bed reactors are used to process fluids which contain suspended solids. Plugging is manifested by an unacceptable pressure drop across the reactor causing premature shutdown, for example, the shutdown of catalytic reactors while usable catalytic activity remains. Granular filter media are used in many industries for the removal of contaminants from liquids.

However, temperatures and pressures, flow velocities, viscosities, fluid properties, and catalyst and suspended solid composition and size distributions are so unique to petroleum refinery processing that unique solutions are sought. For example, while some industries are interested in providing liquids of great clarity, thereby requiring filter techniques for the removal of suspended solids even smaller than 10 microns in diameter, such techniques and filter designs have no application in petroleum refinery packed bed reactor technology where suspended solids of 10 microns in diameter or less cannot plug a reactor containing, for example, catalyst particles of $\frac{1}{8}$ inch in diameter.

However, plugging can be particularly troublesome in downflow packed bed reactors. In the hydrocarbon processing industry, plugging is often encountered in downflow reactors that employ catalysts about $\frac{1}{8}$ inch in diameter or less, e.g., 1/32 to 3/32 inch in diameter.

One technique used in the hydrocarbon processing industry is to employ one or more guard beds above active catalyst particles in order to protect the catalyst from incoming solids in the feed. Such guard beds have had only limited success, however. Even when multiple guard beds are used, catalytic reactors often experience unacceptable plugging, causing premature shutdown. Particularly troublesome is the uneven capture of solids in the guard bed leading to high local concentrations of solids.

One guard bed configuration is described in U.S. Pat. No. 3,562,800 wherein layers of $\frac{1}{8}$ inch and $\frac{1}{4}$ inch aluminum balls are used above a 1/32 inch catalyst bed. The depths of the beds are unspecified, however. Table 1 depicts several guard bed sequences which have been used for downflow packed catalyst beds in the hydrocarbon processing industry.

TABLE I

Configuration	Depth (inches)	Particle Diameters (inches)	Type
A	6-12	$\frac{1}{8}$ - $\frac{1}{4}$	spheres
B	6	$\frac{1}{8}$	saddles
C	6	$\frac{1}{8}$ - $\frac{1}{4}$	spheres
	12	$\frac{1}{8}$	rings
	24	3/16	tablets
D	24	1/3	trilobes
	12	$\frac{1}{8}$	spheres
	12	1/6	spheres
E	4	$\frac{1}{8}$	saddles
	3	$\frac{1}{8}$	spheres
	3	$\frac{1}{8}$	spheres
	3	$\frac{1}{8}$	spheres
	4	$\frac{1}{8}$	saddles

SUMMARY OF THE INVENTION

According to this invention, a systematic method is provided for the design of guard beds for processing hydrocarbonaceous feedstocks. The method results in novel packed bed reactor designs and novel processes for contacting solids-containing feedstocks, in particular, feedstocks contaminated with iron sulfide solids.

In its apparatus aspects, this invention comprises a packed bed reactor for treating a hydrocarbon feedstock containing suspended solids which comprises:

(a) a first packed bed of hydrothermally stable particles in fluid communication with a feed inlet to said reactor, said first packed bed extending more than 3 to 18 inches in the direction of flow and comprising predominantly particles at least about $\frac{1}{8}$ inch in diameter;

(b) a second packed bed of hydrothermally stable particles in fluid communication with the first packed bed and downstream of the first packed bed, said second packed bed extending at least 12 to 48 inches in the direction of flow and comprising predominantly particles having diameters within the range of 3/16 to 5/16 inch and smaller than the average diameter of particles in the first bed; and

(c) a third packed bed of hydrothermally stable particles in fluid communication with the second packed bed and downstream of the second packed bed, said third packed bed comprising predominantly particles having diameters below $\frac{1}{8}$ inch.

In some applications, an additional bed can be placed downstream of the second packed bed and in fluid communication therewith. This additional packed bed will comprise hydrothermally stable particles having diameters within the range of 1/16 and 3/16 inch and smaller than the average diameter of particles in the second packed bed. The third packed bed will be followed by a fourth packed bed in fluid communication with the third packed bed and downstream of the third packed bed and comprising predominantly particles having diameters below $\frac{1}{8}$ inch and smaller than the average diameter of the particles in the third packed bed.

In its process aspects, this invention comprises a process for contacting a fluid hydrocarbon feedstock containing suspended solids which comprises passing the feed through the above-described packed bed reactors under petroleum processing conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 are schematic depictions of a reactor with the guard bed configuration of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Staged filtration of suspended solids is a broad technology wherein specific designs are needed for specific conditions. Impaction theory tends to predict beds which are too shallow to filter solids from a hydrocarbon stream, in particular iron sulfide solids. The present invention provides a deep-bed, guard bed design strategy for high temperature, high pressure hydrocarbon feedstock processing directed toward the removal of suspended solids of greater than 10 microns in diameter from mixed phase gas-liquid-solid, and preferably, wherein said solids are iron sulfide, or have a density similar to that of iron sulfide. Furthermore, in preferred embodiments of this invention, the packed bed which is protected from plugging by the guard bed design of this invention contains particles of less than about $\frac{1}{8}$ inch in diameter. For particles of less than $\frac{1}{8}$ inch in diameter, I find that suspended solids of greater than about 10 microns in diameter form a critical size range which should be removed.

According to this invention, it has been found that a packed bed of particles less than $\frac{1}{8}$ inch in diameter can be protected from plugging by disposing guard beds upstream of the packed bed of particles. The guard beds have a graded particle size which decreases in the direction of flow. The maximum particle size in the guard beds is typically $\frac{1}{8}$ to $\frac{1}{4}$ inches, however, larger particles can be used if desired. The minimum particle size is slightly above the average particle size of the principal contact particles or catalyst in the packed bed being protected.

By "particles" herein referred to is meant the particulate material used as a reactive, catalytic or inert material in guard beds, reactors and filters. Such material, as used in embodiments of the present invention, is preferably mainly composed of porous inorganic oxides such as alumina, titania, clay, and comprises both synthetic and naturally occurring minerals. Such materials must be suitable for petroleum refining processing conditions, i.e., temperatures up to about 1500° F. and pressures up to about 3500 psig. Since petroleum processing conditions of interest are characterized by elevated temperatures and a generally reducing atmosphere, often comprising the presence of hydrogen gas, I refer to materials suitable for the particles of the present invention as "hydrothermally stable". Such petroleum refining processes include both thermal processes and catalytic processes, e.g., visbreaking, hydrocracking, reforming, hydrotreating, sulfur sorbing, hydrofining, etc., any petroleum refining process where a packed bed of particles $\frac{1}{8}$ inch in diameter or less could have increased pressure drop due to the presence of solids, such as iron sulfide, in the feedstream. While "petroleum refining" and "petroleum refining conditions" are referred to herein, it is to be understood that the present invention is applicable to any hydrocarbon feedstock including those derived from shale, coal and tar sands. Furthermore, the solids suspended in the feedstock may be other than iron sulfide and may in the latter instances comprise shale solids, tar sands solids or coal tar particulate and ash. A preferred particulate material for the guard beds would be a spent catalyst particulate from the same refinery. (Of course, the solid suspended in the hydrocarbon feedstock is also a particulate material but I will avoid the use of the word "particle" in reference thereto to prevent confusion.)

Particles will be described herein in terms of their average diameters. While spherical particles are very much preferred for use in the guard bed, the guard bed particles can be in other configurations. For non-spherical particles, the diameter is defined as the smallest diameter, i.e., the smallest surface-to-surface dimension through the center or axis of the particle, regardless of the shape of the particle.

This invention is primarily applicable in downflow packed bed systems. The packed bed can be any gravity-packed bed configuration, for example, a fixed bed, a moving bed, or a bed which permits incremental addition of fresh particles.

The word "fluid", as used herein, encompasses both liquid and gaseous phases. The feeds can be liquid-solids, gas-solids, or gas-liquid-solids, and will generally contain no more than about 0.1 weight percent suspended solids. The most preferred application for this invention is the processing of fluids containing less than 10 ppmw of solids, which is typical of petroleum refinery streams. The optimum guard bed design will depend upon the size distribution of solids in the feedstream. Typical solid size distributions of interest have an average diameter between about 5 to 1,000 microns. Solids smaller than about 10 microns generally do not cause plugging problems in downflow packed beds. Solids above 1,000 microns in diameter generally are easily filtered by conventional means, prior to treatment in packed bed reactors. Solid size distributions suitable for this invention are found in a variety of feeds in the hydrocarbon processing industry. For example, naphtha, vacuum and atmospheric residua, vacuum gas oils, diesel and medium distillate streams, and a variety of other feedstocks, including certain solids-lean synthetic oils derived from coal, oil shale and tar sands, etc. The suspended solid in petroleum-derived streams is primarily iron sulfide from scaling of upstream equipment and piping, however, other solids may be present as well.

This invention employs in part the theory of impaction in packed beds which is described in Jackson et al., "Entrained Particle Collection in Packed Beds", AIChE Journal, November 1966, pages 1075-1078, which is incorporated herein by reference. According to this invention, however, it is found that impaction alone is not adequate to describe the behavior of solids in packed beds. While impaction theory might predict substantially all solids of a certain size should be trapped within the first few inches of a particle bed, it has been discovered that in practical applications solids which have impacted become re-entrained and travel further into the bed to impact other solids. Consequently, the guard beds for trapping the solids need to be significantly deeper than would be expected from impaction theory.

In embodiments of the present invention, the hydrocarbon fluid is subjected to petroleum refining processing conditions. In particular, in embodiments of the present invention, the fluid will preferably move relative to the guard bed particles with a superficial velocity of from about 0.2 to about 0.8 inch per second for up to 90% of the time in the case of a liquid, and of up to about 8 inches per second for up to 90% of the time in case of a vapor. The fluid hourly space velocity in embodiments of the present invention will preferably vary from about 1 to about 100 depending upon the fluid phase and the guard bed length.

It has been found that with typical feed solid size distribution, at least about 10 inches of 3/16 to 5/16 inch

particles are needed in the guard bed. If the depth of the 3/16 to 5/16 inch diameter particle bed is insufficient, solids of the critical size, i.e., larger than 10 microns, will pass through and tend to agglomerate at the interface between that bed and the adjacent bed.

In the ideal situation, a guard bed would have a continuously decreasing particle size including a region 12 to 48 inches or deeper of particles in the 3/16 to 5/16 inch diameter range. In practice, however, such continuously decreasing size is difficult to achieve. Satisfactory results can be obtained with a plurality of discrete guard beds with each bed containing particles of predominantly the same size. Consequently, the term "bed" as used herein will include a region of particles of varying particle size within the particle size limits defined for the bed.

It is conceivable that thin intermediate beds or screens may be disposed between one or more of the guard beds. While the reactor should preferably comprise particles whose diameter decreases essentially continuously in the direction of flow, the thin intermediate beds may contain particles larger than those in one or more of the upstream beds. The thin intermediate beds should not, however, comprise particles smaller than downstream beds, as this will promote uneven solids capture, leading to premature pressure drop build-up.

The number of guard beds and the size of the bed particles will depend upon the characteristics of the feed. The following examples describe the cases of liquid-solid, gas-solid, and gas-liquid-solid feeds. The examples will illustrate the use of inert guard bed particles above catalyst beds; however, it should be understood that the guard bed particles may themselves contain active catalyst materials such as transition metals, etc. The guard bed particles may, in fact, be of the same composition as the main catalyst or contact particles, and may be spent catalyst of said composition.

The designs depicted in the following examples are embodiments of the invention suitable for processing hydrocarbonaceous feedstocks at typical refinery processing conditions, for example, elevated pressures of up to about 3500 psig and elevated temperatures of up to about 1500° F., preferably pressures of 500 to 3000 psig and temperatures of 300° F. to 1200° F., more preferably pressures of 1000 to 2000 psig and temperatures of 600° F. to 900° F. These embodiments are also preferred for the treatment of hydrocarbonaceous feedstocks, and particularly, hydrocarbonaceous feedstock contaminated with iron sulfide solids. Of course, the temperature and pressure in a given guard bed will vary within and between these ranges with time during the same run.

EXAMPLE 1

Liquid-Solid Feed

Referring to FIG. 1, the hydrocarbon feedstock enters the reactor 1 through an inlet and encounters a first packed bed 3 containing particles above $\frac{1}{8}$ inch, preferably $\frac{1}{4}$ to 1 inch, and most preferably about $\frac{1}{2}$ inch in diameter. The first packed bed is more than about 3 inches deep and can extend up to about 18 inches or more in depth, e.g., 24, 36 inches, etc. The preferred depth of the first packed bed is 6 inches. The function of the first bed is to trap large solids and to stabilize the lower beds and protect them from inlet surges, etc. The second packed bed 2 contains predominantly particles in the range of 3/16 to 5/16 inch in diameter, preferably

about $\frac{1}{2}$ inch in diameter. The second packed bed is at least about 12 to 48 inches deep and can be more than 48 inches deep, preferably about 2 feet deep. The main catalyst bed contains cylindrical extrudate catalyst 1/32 to 3/32 inch in diameter, preferably about 1/16 inch in diameter and with a length-to-diameter ratio of from 2 to 10. The main catalyst bed can be any depth. Preferably the first and second beds contain spherical particles. This design is especially well suited for capturing solids with an average diameter of about 5 to 1,000 micrometers, preferably 25 to 250 micrometers average diameter. If most of the feed solids by weight are smaller than 50 microns in diameter, the second catalyst bed can be replaced by about 12 inches of 3/16 to 5/16 inch diameter spheres on top of about 12 inches of 1/16 to 3/16 inch diameter spheres. The additional 1/16 to 3/16 inch spheres should also be used where the main catalyst bed contains catalyst smaller than about 1/16 inch in diameter. If most of the feed solids by weight are larger than 300 microns in diameter, the first catalyst bed should be increased in depth.

EXAMPLE 2

Gas-Solid Feeds

Again referring to FIG. 1, the first particulate bed 3 in this case should contain spheres above $\frac{1}{8}$ inch, preferably $\frac{1}{4}$ to $1\frac{1}{2}$ inches in diameter, and most preferably about $\frac{1}{2}$ inch in diameter. The first packed bed is more than about 3 inches deep and can extend up to 18 or more inches, e.g., 24, 36 inches, etc. The first packed bed is preferably about 9 inches deep. The second packed bed contains predominantly particles 3/16 to 5/16 inch in diameter, preferably about $\frac{1}{2}$ inch in diameter, and should extend from about 12 to 48 inches in depth, preferably about 24 inches. The main catalyst bed is again a cylindrical extrudate catalyst 1/32 to 3/32 inch in diameter, preferably 1/16 inch in diameter, and having a length-to-diameter ratio of 2 to 10. Again, this design is suited for capturing solids of 5 to 1,000 micrometers in diameter, preferably with an average particle diameter of 25 to 250 micrometers. If most solids to be captured by weight are smaller than 50 micrometers, the second packed bed can be replaced by 18 inches of 3/16 to 5/16 inch spheres followed by about 6 inches of 1/16 to 3/16 inch spheres. Also the first catalyst bed can be replaced by about 6 inches of about $\frac{1}{2}$ inch diameter spheres. In gas phase reactors, a number of flakes of sulfides from upstream equipment can be much larger than the remainder of the feed particles. When this condition is encountered or when most of the feed solids by weight are solids larger than 300 micrometers in diameter, the first particulate bed should contain about 12 inches of spheres of about 1 inch in diameter.

If severe plugging problems are expected, an additional bed, about 12 inches deep, of spheres 1/16 to 3/16 inch in diameter can be employed between the second packed bed and the main catalyst bed. The additional bed of 1/16 to 3/16 inch spheres should also be used when the main catalyst bed contains catalyst smaller than about 1/16 inch in diameter.

EXAMPLE 3

Gas-Liquid-Solid Feed

Referring to FIG. 2, the hydrocarbon feed to the reactor 1 encounters the first packed bed 6 which contains particles above $\frac{1}{8}$ inch in diameter, preferably $\frac{1}{4}$ to

1 inch, and most preferably about $\frac{1}{8}$ inch. The depth of the first packed bed is more than about 3 inches, and can be up to 18, 24, 36 or more inches, preferably about 6 inches. The second packed bed 5 contains spheres predominantly $3/16$ to $5/16$ inch in diameter and is 12 to 48 or more inches in depth, preferably about 18 inches in depth. The third packed bed 4 contains particles of $1/16$ to $3/16$ inch in diameter, preferably about $\frac{1}{8}$ inch in diameter. The third packed bed is at least about 3 to 18 or more inches in depth, preferably about 6 inches in depth. The main catalyst bed is preferably cylindrical extrudate catalyst $1/32$ to $3/32$ inch in diameter, preferably about $1/16$ inch in diameter, and having a length-to-diameter ratio of about 2 to 10. Again, this example is well suited for capturing solids with an average size in the range of 5 to 1,000 micrometers, preferably 25 to 250 micrometers in diameter. If most of the solids to be captured by weight are smaller than about 50 micrometers in diameter, the third packed bed 4 should be increased in depth to about 12 inches and the second packed bed 5 can be reduced in diameter to about 12 inches. If most of the solids to be captured by weight are larger than about 300 micrometers, the first catalyst bed should be about 12 inches in depth. Where the main catalyst bed contains particles smaller than about $1/16$ inch in diameter, the third packed bed should be at least about 12 inches deep.

The configurations described in Examples 1 through 3 are primarily suited for reactors which in the absence of the guard bed form undesirable plugs when less than 20% of their normal catalyst life would be utilized. If the reactors would operate substantially more than about 20% of their normal catalyst run life without the guard beds, then the guard bed design could be modified to reduce the depth of particles in the second packed bed, i.e., the $3/16$ to $5/16$ inch particles.

The following experimental results illustrate the drastically improved performance of a downflow cold model pilot plant reactor 4 inches in diameter containing $1/16$ diameter extrudate catalyst. The feed was hexane containing $\frac{1}{2}$ to 1% solids which had been collected from a fouled reactor and which comprised essentially iron sulfide. These iron sulfide solids are representative of the particulate contaminant encountered in commercial practice. Hexane was chosen to approximate the density and viscosity of liquid naphtha at normal process temperature and pressure. The concentration of the feed solids was deliberately much higher than ordinarily encountered in practice in order to reduce the time of the experiment. The results are depicted in Table 2. The reactor loading is in the downward direction.

TABLE 2

Reactor Loading	Collected Solids (lbs./sq. ft.)	Pressure Drop (psi)	Length of Run (min.)
12 inches of $1/16$ inch diameter cylindrical extrudate	3.4*	10	6
12 inches of $\frac{1}{8}$ inch spheres + 12 inches of $1/16$ inch diameter cylindrical extrudate	2.1*	10	4
12 inches of $\frac{1}{8}$ inch spheres + 12 inches of $1/16$ inch diameter cylindrical extrudate	7.6	0.3	16
24 inches of $\frac{1}{8}$ inch spheres + 12 inches of $1/16$ inch diameter	13.9	0.4	21

TABLE 2-continued

Reactor Loading	Collected Solids (lbs./sq. ft.)	Pressure Drop (psi)	Length of Run (min.)
cylindrical extrudate 6 inches of $\frac{1}{8}$ inch spheres + 12 inches of $\frac{1}{8}$ inch spheres + 6 inches of $\frac{1}{8}$ inch spheres + 12 inches of $1/16$ inch diameter cylindrical extrudate	22.8	1.5	43

*Most solids collected in first 2-3 inches of $1/16$ inch catalyst bed.

It is seen that when no guard bed is used, a very low solids loading was obtained, and the 10 psi pressure drop occurred after only 6 minutes of operation. With a guard bed containing only 12 inches of $\frac{1}{8}$ inch spheres, the solids loading was also low and the 10 psi pressure drop occurred after only 4 minutes. With guard beds containing 12 or 24 inches of $\frac{1}{8}$ inch spheres, the solids collection was significantly increased with only a very low pressure drop after much longer run times. The triple guard bed was allowed to operate to a higher solids loading and pressure drop.

Those skilled in the art will recognize that the guard bed design depicted herein can be modified to account for differences in feed solids, etc. without departing from the spirit and scope of this invention. Such modifications are contemplated as equivalent of the embodiments particularly described herein.

What is claimed is:

1. A process for contacting a fluid hydrocarbon feed containing suspended solids comprising passing said feed through a packed bed reactor containing catalyst particles of about $\frac{1}{8}$ inch diameter or less comprising:
 - (a) a first packed bed of hydrothermally stable particles in fluid communication with a feed inlet to said reactor, said first packed bed extending more than 3 to 18 inches in the direction of flow and comprising predominantly particles at least about $\frac{1}{8}$ inch in diameter;
 - (b) a second packed bed of hydrothermally stable particles in fluid communication with said first packed bed and downstream of said first packed bed, said second packed bed extending at least 12 to 18 inches in the direction of flow and comprising predominantly particles having diameters within the range of $3/16$ to $5/16$ inch and smaller than the average diameter of particles in said first bed; and
 - (c) a third packed bed of hydrothermally stable particles in fluid communication with said second packed bed in downstream of said second packed bed, said third packed bed comprising predominantly particles having diameters below $\frac{1}{8}$ inch wherein the packed bed reactor is maintained at elevated pressures of up to about 3,500 psig and elevated temperatures of up to 1500° F.
2. A process according to claim 1 wherein at least one of said first and second packed beds comprises substantially spherical particles.
3. A process according to claim 1 wherein said suspended solids comprise iron sulfide.
4. A process according to claim 1 wherein said feed contains liquid and solids and is passed downwardly through said reactor, said first packed bed comprises predominantly particles within the range of $\frac{1}{8}$ to $\frac{1}{4}$ inch

in diameter, and said third packed bed comprises predominantly particles 1/32 to 3/32 inch in diameter.

5. A process according to claim 1 wherein said feed comprises gas and solids and is passed downwardly through said reactor, said first packed bed comprises substantially particles within the range of $\frac{1}{8}$ to 1 inch in diameter, and said third packed bed comprises particles predominantly within the range of 1/32 to 3/32 inch in diameter.

6. A process according to claim 12 wherein said first packed bed comprises predominantly particles about $\frac{1}{2}$ inch in diameter and second packed bed comprises predominantly particles about $\frac{1}{4}$ inch in diameter.

7. A process of contacting a hydrocarbon fluid feed containing suspended solids comprising passing said feed in a downflow direction through a packed bed reactor comprising:

(a) a first packed bed of hydrothermally stable particles in fluid communication with a feed inlet to said reactor, said first packed bed extending more than 3 to 18 inches in the direction of flow and comprising predominantly particles within the range of $\frac{1}{8}$ to 1 $\frac{1}{2}$ inches in diameter;

(b) a second packed bed of hydrothermally stable particles in fluid communication with said first packed bed and downstream of said first packed bed, said second packed bed extending at least 12 to 48 inches in the direction of flow and comprising predominantly particles having diameters within the range of 3/16 to 5/16 inch and smaller than the average diameter of particles in said first bed;

(c) a third packed bed of hydrothermally stable particles in fluid communication with said second packed bed and downstream of said packed bed, said third bed extending 3 to 48 inches in the direction of flow, said third packed bed comprising predominantly particles having diameters within the range of 1/16 to 3/16 inch and smaller than the average diameter of particles in said second bed; and

(d) a fourth packed bed of hydrothermally stable particles in fluid communication with said third packed bed and downstream of said third packed bed, said fourth packed bed comprising predominantly particles having diameters below $\frac{1}{4}$ inch and smaller than the average diameter of particles in said third packed bed and wherein the packed bed reactor is maintained at elevated pressures of up to about 3,500 psig and elevated temperatures of up to 1500° F.

8. A process according to claim 7 wherein at least one of said first and second packed beds comprises substantially spherical particles.

9. A process according to claim 7 wherein said feed comprises liquids, gas and solids and is passed downwardly through said reactor, said first packed bed comprises predominantly particles within the range of $\frac{1}{8}$ to $\frac{1}{2}$ inch in diameter, said third packed bed comprises predominantly particles within the range of 1/16 to 3/16 inch in diameter, and said fourth packed bed comprises particles predominantly within the range of 1/32 to 3/32 inch in diameter.

10. A process according to claim 9 wherein said first packed bed comprises predominantly particles about $\frac{1}{2}$ inch in diameter, said second packed bed comprises predominantly particles about $\frac{1}{4}$ inch in diameter, and said third packed bed comprises predominantly particles about $\frac{1}{8}$ inch in diameter.

11. A process according to claim 4 wherein said fluid feed contains less than 0.1% by weight solids and said solids in said feed have an average diameter in the range of 25 to 250 micrometers.

12. A process according to claim 7 wherein said fluid feed contains less than 0.1% by weight solids and said solids and said feed have an average particle diameter within the range of 25 to 250 micrometers.

13. A process according to claim 11 wherein said feed contains less than 10 ppm by weight solids.

14. A process according to claim 12 wherein said feed contains less than 10 ppm by weight solids.

* * * * *

B

Selecting the catalyst configuration

After the mathematical model of the catalyst and reactor has been developed, the next step in engineering a catalyst is to select the pellet's size, shape, average pore size, and pore-size distribution.

James W. Fulton, Monsanto Co.

A catalyst pellet's shape and dimensions should promote catalytic activity, strengthen the pellet's resistance to crushing and abrasion, minimize bed pressure drop, lessen fabrication cost, and distribute dust buildup uniformly. Unfortunately, these objectives are not easily achieved. Indeed, several are mutually exclusive. For example, a smaller size will enhance activity but also increase bed pressure drop. The best operational catalyst, therefore, is the shape and dimensions that, in the end, represent the maximum economic tradeoff.

Guides to shape and size selection

Catalytic material can be supported on a carrier pellet, or formed directly into pellets — i.e., the catalytic material itself (e.g., an oxide powder) can be extruded or tableted. (These operations will be discussed in Part 3.) Whereas the shapes into which the catalytic material alone can be formed are limited, the shapes possible for supported catalysts are virtually infinite. (Only a few variations are shown in Fig. 1.)

However, many of the shapes can be eliminated because they would not have the structural strength to resist crushing and abrasion, or would not be easy to fabricate. For example, several in Fig. 1 have sharp corners, which would soon crumble in service. The resulting dust and fragments would plug the spaces between pellets, and cause premature buildup in bed pressure drop. Several others could not be extruded, or even tableted. (Minimum fabrication cost often mandates that pellets be extruded rather than tableted.)

It would take forever to evaluate every possible shape. Nature, however, offers guidance. The single element that, giving the minimum amount of material, affords the maximum strength and abrasion resistance, yet is easily extruded, is the hollow cylinder (e.g., plant stems and animal bones). (Inciden-

This time-part Refresher series on Catalyst Engineering is intended for engineers who chemical processing companies. Although the series will address all catalyst aspects, chief among its purposes is to assist engineers in working with a catalyst manufacturer to develop the optimum gas-phase heterogeneous catalyst for a plant reaction process. For an outline of all the parts of this series, see the Feb. 17 issue, p. 118.

— Building the mathematical model of the catalyst and reactor — appeared in the Feb. 17 issue, p. 118. It presented mathematical correlations for quantifying the phenomena that govern the performance of a catalyst and reactor.

— Making the catalyst — will appear in the July 7 issue. It will deal with the factors involved in choosing the appropriate method for fabricating, drying and loading a catalyst, all of which affect its performance.

For information about the author, see the Feb. 17 issue, p. 124.

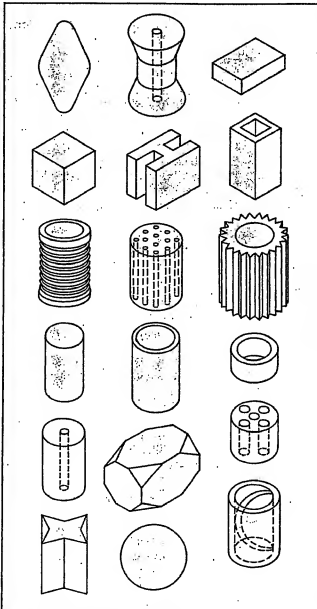


Figure 1 — These catalyst pellet shapes represent only a few of the almost limitless variety possible

tally, the strongest massive natural structure that uses the minimum amount of material is the honeycomb.) Therefore, an obvious choice of pellet shape is the hollow cylinder.

The size, as well as the shape, of a porous catalyst pellet determine the pore length required for the diffusion of product and reactant gases. This diffusion length, in turn, influences the overall rate of reaction. The relationship between diffusion and reaction rate is correlated by an effectiveness factor, shown at the upper part of Fig. 2 for an example system. The lower part of Fig. 2 demonstrates, via experimental data, the strong influence of catalyst shape and dimensions on the overall activity of this example system.

As material is removed from inside a pellet, the pore length for diffusion decreases, thereby increasing the mass transfer rate. This enhances the pellet's effectiveness. Ultimately, re-

moving material from inside the pellet reduces the reaction rate per unit volume of reactor because less catalyst is available. Thus, the tradeoff between pore length and quantity of material must be optimized.

The removal of material from the inside of a pellet reduces its crush strength. In Fig. 3, for instance, 3b might be an improvement over 3a, but 3c might not be better than 3a because crush strength is reduced and too much material is lost. One improvement on the hollow cylinder is shown in Fig. 3e. It reduces pore length for diffusion but adds strength to the thinner wall.

Removing material from the outside of a pellet (i.e., making the pellet smaller) also reduces pore length and enhances effectiveness. Unfortunately, the smaller size increases the pressure drop through the bed and, thereby, the cost of power

Nomenclature

A_{cs}	Bed cross-sectional area, cm^2
a	Diffusion parameter defined by Wakao and Smith [16]
a_F	Arbitrary constant specific to a catalyst that must be determined experimentally
C_{DB}	Concentration of dust on bed particles, g/cm^3
$(C_{DB})^0$	Concentration of on inlet bed particles, g/cm^3
C_{DG}	Concentration of dust in gas, g/cm^3
$(C_{DG})^0$	Concentration of dust in inlet gas, g/cm^3
D_{eff}	Effective pore diffusivity, cm^2/s
D_{ij}	Binary bulk diffusivity, cm^2/s
D_M, D_m	Diffusivity in, respectively, macropores and micropores, cm^2/s
D_M', D_m'	Mean Knudsen diffusivity of gas A in, respectively, macropores and micropores, cm^2/s
d_i, d_o	Hollow pellet diameter, internal and external, respectively
d_p	Catalyst pellet dia., cm
E_m	Effectiveness factor for microporous powder particles
F_V	Volumetric feedrate, cm^3/s
G	Gas superficial mass velocity, $\text{g}/(\text{cm}^2)(\text{s})$
g_c	Force constant, g/s^2
h	Thiele modulus of a solid pellet; in Eq. (4), equal to $(k/D_{eff})^{1/2}$
h'	Thiele modulus of a hollow pellet; in Eq. (8), equal to $(V_h/S_h)(k/D_{eff})^{1/2}$
h_B	Bed height, cm
k	Reaction rate constant, s^{-1}
k_F	Filtration constant
ΔP	Pressure through packed bed of catalyst pellets, $\text{gram-force}/\text{cm}^2$
S_h	External surface area of a hollow pellet, cm^2
t	Time, min
u_g	Gas superficial velocity (equal to F_V/A_{cs}), cm/s
V_h	Volume of catalytic material in a hollow pellet, cm^3
V_s	Volume of pellet not having a hollow portion, cm^3
x	Distance through a bed, cm
y	Mole fraction of reactant gas in macropores
Greek letters	
ϵ_B	Bed void fraction for solid-cylinder pellet; for hollow-cylinder pellet, equal to $0.4 + 0.6 (d_i/d_o)^2$ assuming intrareactor void fraction is 0.4
ϵ_M, ϵ_m	Porosity (void fraction of the total pellet) in, respectively, macropores and micropores
ϵ_p	Catalyst pellet void fraction
η	Catalyst effectiveness factor
η_m	Effectiveness factor for the micropores
ϕ_B	Fraction of the packing by which the gas passes, an arbitrary constant
μ_g	Gas viscosity, poise
ρ_g	Gas density, g/cm^3

delivering a constant feedrate. Again, a tradeoff must be optimized. Economics, the key to optimizing these tradeoffs, are discussed fully in Part 5.

Selecting the catalyst's support

Supports for catalytic materials are frequently a refractory material shaped into a sphere, cylinder, ring or one of a variety of other forms. The catalytic agent is added to the support, either uniformly distributed throughout the pellet (most commonly) or as a coating on the outer surface (especially if the catalyst is expensive — platinum, palladium, etc.).

Supports for plant catalysts are primarily of alumina, silica, activated carbon or diatomaceous earth. Alumina is the most widely used. Inexpensive and of high purity, it is available in several forms and a variety of pore-surface areas. The low

pore-surface area ($<15 \text{ m}^2/\text{g}$) α -alumina is rugged and can hold up under the extreme stress of, for example, natural-gas steam reforming and certain oxidizing conditions. The high pore-surface area (up to $200 \text{ m}^2/\text{g}$) γ -alumina is well suited as a support for mixed and precipitated plant catalysts. Certain forms of alumina are weakly acidic and possibly catalytic.

A number of factors must be considered when choosing a support, such as its inertness or activity; influence on the properties of the catalytic material and promoters; surface area, which can be in macropores or micropores, or both; porosity (the amount of open volume in the pellet), which is related to surface area (average pore size and pore-size distribution are important variables); adsorptive properties relative to the catalytic material, reactants and products, poisons, etc.; thermal resistance to pore collapse, sintering and other struc-

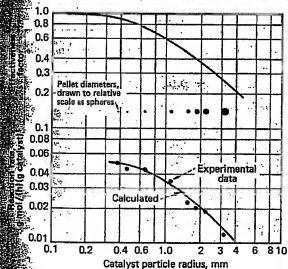


Figure 2 — Effectiveness factor and reaction rate decline with increasing pellet size

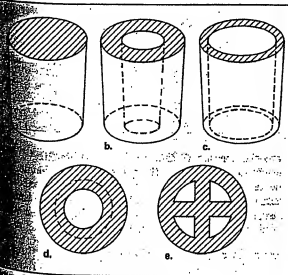


Figure 3 — Tradeoffs determine the optimum shape and size of catalyst pellet

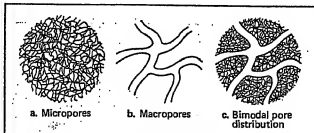


Figure 4 — Bimodal pore distribution gains the advantages of small and large pore sizes

tural degradation; chemical stability; catalyst pellet size and configuration; compressive strength, hardness, and resistance to attrition; stability under anticipated operating conditions; and cost.

A broad review of catalyst supports has been made by Satterfield [11] and Moss [8]. The selection of supports from a reaction engineering point of view has been examined by Shingu and Inui [12]. The desired characteristics of catalyst supports, as well as a useful questionnaire for designing them, have been presented by Trimm [15]. The design and preparation of supported catalysts, especially the dispersion of the material on the support, have been discussed by Acres, et al [1]. Patents on the manufacture of shaped catalyst particles have been reviewed by Sittig [14].

Pore size and pore-size distribution

A catalyst pellet having a large surface area is necessarily composed of small pores (Fig. 4a). High surface area is desirable because less reactor volume is required. However, small pores hinder pore diffusion by reactants and products. The overall result could be a reaction system in which a slow mass-transfer rate within the pores controls the reaction rate.

On the other hand, a pellet having large pores (Fig. 4b) would allow rapid pore diffusion, and reaction kinetics would be rate-controlling. However, if the pores were large, surface area would be small. Overall, the catalyst could be "inactive." This could be avoided by designing the pore size to exactly balance the mass-transfer and reaction-kinetics rates, so that neither slowed the reaction rate. However, this is not easily done. An easier solution is to design the pellet so that it has both large and small pores (Fig. 4c).

The optimum pore size and pore-size distribution for a

particular reaction system can be determined beforehand by testing parameters with the mathematical model of the reactor. Pore-size and pore-size distribution can be varied to seek the most economical process overall.

The preparation of this model involves two major correlations: intrinsic reaction-rate equations, and diffusivities of the reaction molecules in the pores (i.e., Fick's diffusion coefficients for macropores, and Knudsen's for micropores). By means of these correlations, the reaction system can be modeled, and the model used to explore the influence of pore size and pore-size distribution. Doing this can save countless hours and dollars of research, even though the choice indicated would have to be verified experimentally.

The influence of pore diffusion is most readily established by means of the effectiveness factor, which is multiplied by the

Effective diffusivity in a porous pellet may also be a function of the reaction rate (i.e., pore mass transfer and reaction kinetics interact to influence effective diffusivity), as demonstrated by Wakao and Smith [16], who derived a correlation for effective diffusivity, assuming a first-order (or pseudo-first order) and reversible reaction:

$$D_{eff} = \frac{\epsilon_M^2}{1 - \alpha y} + \left[\frac{\epsilon_M^2 (1 + 3\epsilon_M)}{1 - \epsilon_M} \right] \frac{E_m D_m}{D_M'}$$

Assuming a first-order reaction, Ors and Dogu [8] developed an effectiveness-factor model for bidispersed pores with the interaction of kinetics and mass transfer. Pore structure and impregnation characteristics of pelleted catalysts

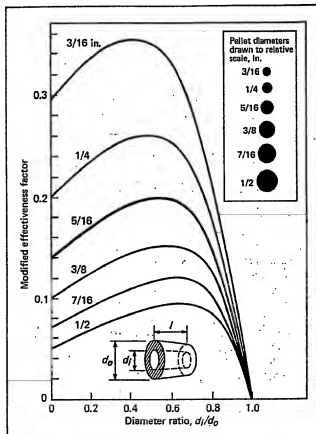


Figure 5—Overall effectiveness of ring catalyst ($l/d_o = 1$) varies with d_i/d_o ratio

intrinsic reaction-rate equation to get the overall reaction rate. Several methods of incorporating pore size and pore-size distribution in the effectiveness factor have been proposed. The simplest, most straightforward, and most easily generalized one is for bimodal pore-size distribution, in which the overall effective diffusivity in the Thiele modulus is given by:

$$D_{eff} = \epsilon_M D_M / 2 + (\epsilon_M D_M / 2) \eta_m \quad (1)$$

The value of η_m may need to be determined by trial and error: first assume that $\eta_m = 1$, then modify it's value until the correlation satisfies the data.

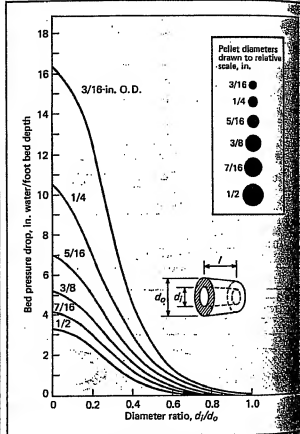


Figure 6—Ring-catalyst ($l/d_o = 1$) pressure drop declines with increasing diameter ratio

automobile emission control were optimized by Hegedus whose model also included the expected penetration depth of the catalyst poison. The results strongly favored bimodal density catalyst structures. The influence of bulk and Knudsen diffusion on the effectiveness factor for the steam-methane reforming reaction has been illustrated by Gonzalez, et al.

Relationship between effectiveness and diffusivity
The performance of a porous catalyst depends on the influence of intrapellet diffusion, which is correlated by the effectiveness factor: η = actual reaction rate/reaction rate without

of pore diffusion. As the pore length for diffusion is increased, the effectiveness factor increases, to a maximum of 1.0. For example, as the diameter of a pellet is reduced, η increases as shown in Fig. 2.

For a pellet shaped as a hollow cylinder, η increases as the hole diameter is increased relative to the outer diameter. However, this reduces the quantity of catalyst that can be packed into a reactor. Thus, optimum reactor performance (i.e., maximum effectiveness) depends on the best tradeoff between catalyst effectiveness and catalyst volume [Eq. (5)].

Overall effectiveness of a catalyst shaped as a hollow cylinder has been correlated by Basmadjian [2]:

$$E' = (1 - \epsilon_B)(V_H/V_P)(1/h)(\tanh h') \quad (3)$$

where h' is the length of the hollow cylinder is twice its diameter:

$$h' = \frac{2}{h} \left[\frac{(1 - \epsilon_B)(1 + d_f/d_o)(1 - d_f/3d_o)}{\tanh \left[\left(\frac{1 - d_f/d_o}{1 - d_f/3d_o} \right) h \right]} \right] \quad (4)$$

Pressure drop through a packed bed

The pressure drop through a packed bed of pellets, in g/cm^2 , can be found by means of the Ergun correlation [10]:

$$\Delta P = h_B \left(\frac{1 - \epsilon_p}{\epsilon_p^3} \right) \left(\frac{G^2}{d_p \rho_p} \right) \left[\frac{150(1 - \epsilon_p)\mu_g}{d_p G} + 1.75 \right] \quad (5)$$

Because the first part of the third term is negligible [5] (it can be expressed for laminar resistance), Eq. (5) can be reduced to:

$$\Delta P = h_B \left(\frac{1 - \epsilon_p}{\epsilon_p^3} \right) \left(\frac{G^2}{d_p \rho_p} \right) \left(\frac{1.75}{\phi_B^2} \right) \quad (6)$$

For hollow cylinders, $\phi_B = 0.6$ [5]. A correlation with pressure-drop data of Norton Co. for hollow cylinders confirmed this 0.6 figure, with the bed void fraction expressed as:

$$\epsilon_p = 0.45 + 0.55 (d_f/d_o)^3 \quad (7)$$

For ϵ_B — i.e., the catalyst-bed void fractions are calculated differently for pressure-drop and reaction computations; compare Eqs. (3) and (7). The $0.55(d_f/d_o)^3$ term in Eq. (7) is required to accurately correlate the pressure-drop data. For reaction computations, the solid fraction of the bed, which is $(1 - \epsilon_p)V_H/V_P$, is given by $(1 - \epsilon_p)V_H/V_P$. The influence of pellet d_f/d_o on bed pressure drop is shown in Fig. 6.

Bed buildup boosts pressure drop

Particulate may enter the reactor from upstream processes (adsorption columns, guard beds, etc.) in the form of precipitates, polymer residues, etc. It will be distributed throughout the reactor with the higher concentration near the entrance of the reactor. Both the quantity and the distribution of dust in the reactor are critical to reactor performance.

The mathematical correlations for dust collection in a fixed bed are derived from filtration theory. Several mechanisms influence filtration rate: inertial impaction by the particles on the catalyst pellets, agglomeration, settling, Brownian dif-

fusion, and electrostatic deposition. In packed beds, the accumulation of dust on the pellets is due primarily to the first of these. The dust in the stream strikes the pellets because of the particles' inertia (i.e., they cannot flow around the pellets with the gas).

From filtration theory [6,12]:

$$C_{DB}/(C_{DB})^0 = \exp(-\alpha_F u_g x / \mu_p) \quad (8)$$

Assuming first-order adsorption kinetics, a material balance on the dust accumulated on the catalyst bed gives:

$$dC_{DB}/dt = k_F C_{DG} \quad (9)$$

For a constant dust concentration in the feed gas:

$$(C_{DB})^0 = k_F (C_{DG})^0 t \quad (10)$$

Substituting:

$$C_{DB} = k_F (C_{DG})^0 \exp(-\alpha_F u_g x / \mu_p) t \quad (11)$$

The void fraction at any bed depth and time, ϵ_D , is found by subtracting the dust concentration from the initial void fraction, ϵ_0 :

$$\epsilon_D = \epsilon_0 - k(C_{DG})^0 \exp(-\alpha_F u_g x / \mu_p) t \quad (12)$$

This void fraction, ϵ_D , should be used in Eq. (5) to determine pressure drops across differential sections through the catalyst bed. These differential pressure drops are then summed or integrated to get the total pressure drop through the bed.

Jay Matley, Editor

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PTO 2000-2748

Germany
3,539,195



HYDROPROCESSING CATALYZER WITH SPECIFIC GEOMETRIC SHAPE
[Hydroprocessing-Katalysator bestimmter geometrischer Gestalt]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. May 2000

Translated by: Schreiber Translations, Inc.

Country : German

Document No. : 3,539,195

Document Type : Patent application

Language : German

Inventor : Chi-Wen Hung and John A. Zakarian

Applicant : Chevron Research Co.

IPC : B01J 35/02

Application Date : 05 November 1985

Publication Date : 07 May 1986

Foreign Language Title : Hydroprocessing-Katalysator
bestimmter geometrischer Gestalt

English Title : HYDROPROCESSING CATALYZER WITH
SPECIFIC GEOMETRIC SHAPE

The invention concerns hydroprocessing or hydrotreatment catalyzers which are useful especially for diffusion-limited reactions. They comprise extrudates with a cross section that is oval and has two holes therein.

Utilization: Hydroprocessing of heavy oil fractions as well as heavy oil residues.

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Hydroprocessing Catalyzer with Specific Geometric Shape

1. Hydroprocessing catalyzer with specific geometric shape which comprises elongated extrudates of catalytic material, characterized in that the catalytic material comprises a fire-retardant inorganic oxide carrier material and at least one element, or the oxide or the sulfide thereof, which is selected from the groups VIa (corresponding to VIb, which is commonly used in the Anglo-saxon literature) and VIII of the periodic system of elements, wherein the element or elements are present in a proportion of 5 to 35 wt.-% (calculated as the reduced element) of the catalyzer carrier material, wherein the extrudates have cross sections which are oval and have two holes therein. *nickel
cobalt*
2. Catalyzer according to claim 1, characterized in that the cross section can be defined by a rectangle with a width of between 4 and 10 mm and a depth of between 3 and 6 mm. /2
3. Catalyzer according to claim 1, characterized in that at least 80% of the catalyzer volume are located within 1 mm of an extruded surface.

4. Catalyst according to claim 1, characterized in that the surfaces/volume ratio amounts to between 5 and 50 cm⁻¹.
5. Catalyst according to claim 1, characterized in that the catalytic surface extension or the jacket surface amount to more than 200 m²/g and the average pore diameter amounts to between 100 and 700 Å.
6. Catalyst according to claim 1, characterized in that the oval cross section is provided with at least one rib on the same.
7. Process for hydroprocessing hydrocarbon-containing raw materials wherein the raw materials are treated with hydrogen under hydroprocessing or hydrotreatment conditions in the presence of a catalyst, characterized in that the catalyst comprises elongated extrudates of a catalytic material in fire-retardant inorganic oxide carrier material and an element or the oxide or the sulfide thereof, which is selected from the elements of the groups VIa (corresponding to VIb) and VIII of the periodic system of elements, wherein the elements are present in 5 to 35 wt.-% (calculated as the reduced element) of the catalytic material and the extrudates have a cross section which is oval and has two holes. /3
8. Process according to claim 7, characterized in that the hydroprocessing conditions have an hourly liquid space speed

of between 0.05 and 25 h⁻¹, a temperature of between 200 and 500°C, a pressure of between 1.4 and 70 MPa, and a hydrogen/raw material ratio of between 90 and 900 Norm L/L.

Description

/4

The invention concerns so-called hydroprocessing catalyzers or hydrotreatment catalyzers, in particular catalyzers for utilization with diffusion limitation reactions or diffusion limiting reactions.

Catalyzers for hydroprocessing hydrocarbon raw materials have been produced in many shapes and sizes. Under "hydroprocessing" is understood the reaction of a raw material with hydrogen (or a hydrogen-containing mixture) usually in the presence of a catalyzer. Typical hydroprocessing reactions comprise: hydrosulfuration, hydronitrification, and hydrometallization and hydrocracking; two or several of these reactions can run simultaneously (in the same reactor and/or in the presence of the same catalyzer).

Usually, these catalyzers are produced in spherical or cylindric shape. Lately, however, the shape and measurements of the catalyzers have changed to produce a greater catalyzer activity and less rapid deactivation. This is valid in particular if secondary sources such as residues, slate oil, etc. are hydrotreated, because a more extensive hydroprocessing becomes necessary.

It is known that an increased catalyzer activity results in a reduced particle size. However, it is also known that a reduction of the size leads to an increase in pressure drop over the catalyzer bedding. In this way, there is a minimum particle size which can be practically used by utilizing the usual shapes. The utilization of irregular shapes was considered to bring to a minimum a tight packing of the catalyzer beddings. This, however, leads generally to a loss of catalytic effectiveness of the bedding and has been found to be unfavorable in the industry. /5

Different catalyzer shapes have already been proposed. United States patent 2,408,164 (Foster) describes shapes of solid and hollow cylinders, elongated star shapes, cylinders with waved edges, etc. and similar catalyzer shapes have also been described in United States patents 3,997,426 (Montagna et al) and 4,441,990 (Huang). United States patent 3,9⁶~~9~~6,644 (Gustafson) shows a trilobal catalyzer. United States patents 3,674,680 and 3,764,565 (Hoekstra and Jacobs) disclose different shapes, which are designed so that they can remove catalyzer material of more than 0.38 mm from the catalyzer surface. United States patent 3,347,798 (Baer et al) describes hollow pearl catalyzers, while United States patent 3,957,777 (Frayer et al) has as its object amorphous-configured catalyzers. United States patents 4,116,819 and 4,133,777 (Frayer et al) disclose grooved cylindric

extrudates, while United States patent 4,391,740 (Gibson) has as its object extruded catalyzers with "plump oval" cross section. These patents and others cited in this application are expressly included by reference in the disclosure of this application. Catalyzer shapes should be attained, which are suitable for the hydroprocessing or hydrotreatment of petroleum and which are effective in particular for diffusion-limited reactions, and

which can be easily produced. This object is attained according to the invention via a hydrocarbon hydroprocessing or hydrotreatment catalyzer which consists of elongated extrudates of a catalytic material, wherein the catalytic material comprises a fire-retardant inorganic oxide base and at least one element or oxide or sulfide selected from the elements of the groups IVA (corresponding to IVb) and VIII of the periodic system of elements, wherein these elements are present in 5 to 35 wt.-% (calculated as reduced element) of the catalyzer base and these extrudates have a cross section which is oval and is provided with two holes. /6

In a further development of the invention, the invention concerns a process for hydroprocessing or hydrotreating hydrocarbon-containing raw materials, in particular of distillation residues,

by using the above-catalyzers catalyzer.

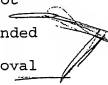
The invention will be further described with reference to the drawings, wherein

- Fig. 1 shows a first embodiment of the hollow oval catalyzer according to the invention, wherein the outer and inner cross sections of the catalyzer are oval;
- Fig. 2 shows an alternative embodiment wherein one of the outer surfaces is elliptic, the inner surfaces have circular cross section; and
- Fig. 3 shows another embodiment wherein the outer surfaces are equipped with ribs and the inner surfaces have an elliptic cross section.

Shape

The catalyzer according to the invention can be generally described as an extrudate with a cross section which is oval and which has two holes therein. Under "oval" is understood a shape which comprises two half circles which are connected via straight-line segments, an ellipsis or an ellipsoid, or other similar shapes that are popularly described as "oval," that is, shapes with two areas of relatively great curvature separated by two areas with relatively less curvature should also be comprised therein.

The areas of greater curvature and/or lesser curvature do not have to consist of individual curves. A rectangle with rounded corners, for example, would also fall under the meaning of oval as it is used herein even though a square with rounded corners would not be included herein. The shape, however, is generally



not necessarily bilaterally symmetric around a plane, which is generally vertical to the areas with less curvature near their center points; they can, however, also be two-sided symmetric around a second plane vertical to the first and can pass through the areas of greater curvature near their center points. 5

Both holes can have cross sections which are circular or oval as was defined above. The holes are positioned in the cross section shape generally in such a way that a maximum symmetry is offered, while ensuring that an adequate thickness of the catalyzer material is available between one hole and another hole on the 10 catalyzer surface to ensure the necessary strength.

The areas of lesser curvature, in particular when they are flat, can be provided with ribs, typically with semicircle-shaped cross sections, which project from the area or areas at one or both sides of the catalyzer particles. These eventually available ribs are arranged in such a way that they do not come to lie over a hole but rather overlap between the holes. In this way is obtained a maximum strength. The also present ribs delimit the approximation of the one particle to the other and delimit in this way a narrow package and the assigned increased pressure drop in a packaged catalyzer bedding. 18

The figures show specific exemplary catalyzer shapes according to the invention. The catalyzer shown in Fig. 1 has an outer cross section which is described popularly as an oval, namely two

semicircle-shaped arches connected by straight lines. The holes are also oval. The cross section has here two symmetric planes. The catalyzer of Fig. 2 has a flat surface and an elliptic surface, while the holes are circular-shaped and the cross section has one plane. The catalyzer of Fig. 3 is similar to the one of Fig. 1, but the oval outer surface is provided with two ribs which are arranged between the holes, while the holes themselves are elliptical. For the expert it is clear when observing this disclosure that other embodiments aside from those described expressly herein and/or described within the frame of the disclosure of the invention are possible. Such shapes are to be considered included within the scope of protection of the invention.

The catalyzer shapes according to the invention are free of sharp corners, be they convex or concave, and in the widest possible range. This means a considerable advantage with respect to the easier production since

- (a) the production of the form plate used for exploding the catalyzer is simplified,
- (b) the abrasion is reduced, with would otherwise occur at the sharp corners, and
- (c) the shape change of the catalyzer extrudate is brought to a minimum, while the shape production plate is abraded.

Measurements

As can be seen in the figures, the catalyzer shapes in general are defined by a right parallelepiped (a rectangular box) with a length L , a width W_e , and a depth D_e , while both holes can be defined by L , W_i , and D_i . L , the length of this extrudate, can be adjusted in that the extrudate is cut in length while it is extruded or can be varied due to natural breaking of the extrudate during production. W_e lies typically in the order of magnitude between 3 and 10 mm, preferably between 4.5 and 8 mm, while D_e typically lies between 2.5 and 6 mm, preferably between 4 and 5 mm. The ratio W_e/D_e amounts typically between 1.2 and 4, preferably between 1.4 and 3, in particular between 1.6 and 2.2. The measurements were selected inter alia in dependence upon the storage of the catalyzers which are used for the hydrotreatment (hydroprocess).

If the catalyzer is provided with ribs, then these have preferably a standing height above the surface from which the project, as shown in Fig. 3, of less than $0.5 D_e$ and preferably $0.15 D_e$ to $0.25 D_e$. The ribs can be provided on one or both sides of the oval. W_i and D_i are selected so that an adequate ¹⁹ inner surface area (of course this will increase with W_i and D_i) ²⁰ as well as an adequate mechanic strength of the particles (adequate thickness of the catalyzer material) is afforded. For example, a particle with $W_e = 9$ mm and $D_e = 4$ mm with a shape consisting of semicircular arches with a diameter D_e connected

via straight lines having a length $(W_0 - D_0)$, as shown in Fig. 1, have oval holes with $W_1 = 3$ mm and $D_1 = 2$ mm, wherein at least a thickness of 1 mm catalyzer material is allowed between and around the holes. /10

Arranging two holes allows a better access to the catalyzer material in the inside of the particle; it is preferred that at least 80%, preferably at least 90%, of the catalyzer volume lies within 1 mm, even more preferred within 0.75 mm, and in particular within 0.50 mm of an extruded (outer or inner) surface. The experts in the field are capable of providing, in view of this disclosure, suitable shapes and measurements for the special application cases and catalyzer materials.

Hollow Fraction

The hollow fraction represents the narrowness of the particle package which can be obtained with particles of a specific shape. In the given space volume can be packed a specific number. If the geometric volume of the particle is multiplied by the number of particles, one obtains a total geometric particle volume V_p . If the volume of the space is V_s , then a hollow space V_v exists, which actually is not taken up by catalyzer particles. In this way is valid that $V_s = V_p + V_v$. The hollow space fraction E , which is assigned to a given shape, results from:

$$E = V_v/V_s = V_v/(V_v + V_p)$$

The lower E is, the greater is the catalyzer quantity needed for contact; a lower E , however, is usually assigned to a higher pressure drop (for otherwise similar catalyzers) over the catalyzer bedding, since a smaller volume is present, through which the treated material can flow. A blocking of the intermediate space is a problem, a high E is desirable. /11

The catalyzer particles according to the invention have an empty space or hollow fraction E between 0.25 to 0.60 fold, preferably between 0.35 and 0.50 fold of the above-given measurements. It is clear that the hollow fraction is greater than the one for a catalyzer without holes, for example, the catalyzers according to United States patent 4,391,740.

Concavity Index

A geometric solid body is convex when all pairs of points which lie within or on the cross section surface of the solid body can be connected by means of a straight line which is completely contained within or on this surface independently from any holes that may pass through the surface. On the contrary, the solid matter is concave when pairs of points can be connected via a straight line which are not completely contained within or on the surface of the solid matter. The volume of a convex solid matter of minimum size which is necessary to obtain a concave solid matter is greater than the volume of this concave solid body. If V_x is the volume of the minimum convex solid matter and V_c is the

volume of the comprised concave solid matter, then the concavity index is given by the expression

$$C = V_x/V_c$$

For a solid matter to be concave, C must be greater than 1 (C is equal to 1 for a convex solid matter).

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Even though different types of concave matter for catalyzer shapes have been suggested (see, for example, United States patent 3,966,644), the catalyzer shape according to the invention is convex at least within the area of the rectangle ($W_s \times D_s$).

If the catalyzer surface is provided with one or several ribs, as shown in Fig. 3, then it becomes concave; the shape when the ribs are missing, however, will be convex. If the surface is concave due to the rib or ribs, then the concavity index is preferably less than 1.2, in particular less than 1.1.

Surface to Volume Ratio

The catalyzer particles according to the invention have a characteristic and geometric surface area and a geometric volume (without taking into consideration the influence of the catalytic assigned pores) which depend from their cross section shape and length. The geometric expansion as well as the geometric volume can be easily computed from the measurements which are assigned to the perfect geometric shapes. Currently available catalyzer particles approximate these shapes and their surface expansions

and volume can be estimated from the geometric models. The ratio of surface expansion to volume, S/V , denotes the particle size and shape.

Generally, an enlarged surface/volume ratio is assigned a higher activity, in particular in a diffusion-limited situation; but it is also assigned a higher pressure drop (other variables are otherwise equal). For diffusion-limited reactions (diffusion-limited reactions), designated above as diffusion-limited reactions, for example a residue hydroprocessing, a higher surface/volume ratio is desirable since the selection of the catalyzer shape/size is generally limited by the allowed reactor pressure drop, generally assigned to a higher hollow space fraction. For non-diffusion-limited reactions, the S/V can be less, with a lower E for an equivalent pressure drop. For the catalyzer particles according to the invention, the S/V lies preferably between 5 and 50 cm^{-1} , in particular between 10 and 30 cm^{-1} .

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In addition to the geometric considerations with respect to particle size and shape, the catalyzer particles must also have certain characteristics, which are assigned to the catalytic effect.

Catalytic Surface

The catalytic surface (jacket surface) is expressed in m^2/g and can be set, for example, by the nitrogen absorption (BET

process). The jacket surface should be greater than 100 m²/g, and preferably greater than 200 m²/g, and in particular approximately 250 to 350 m²/g.

Catalytic Pore Volume

The catalytic pore volume of a catalyzer has per se an inner hollow space. The measurements are usually undertaken by means of a mercury porosymmetry by using pressures of up to 345 mPa. This process determines the pore volume; the pore diameters are usually computed with the equation:

$$D = 4 \times 10^4 \times P/A$$

wherein D is the average pore diameter in A, P is the pore volume in cm³/g, and A is the surface expansion (jacket surface) in m²/g. /14

The catalyzer particles according to the invention can have different jacket surfaces and pore volumes in accordance with their composition and their intended use, but have typically an average pore diameter of between approximately 100 and 700 Å, preferably between 120 and 200 Å, for hydrodemetallization catalyzers and somewhat lesser values for hydrosulfuration catalyzers. The catalyzers can have macropores (pores with a diameter of more than 1000 Å) if desired.

In addition to the above-named characteristics, the catalyzer particles can have specific properties of the composition as mentioned below.

Composition

The catalyzer particles comprise typically a fire-retardant of inorganic oxide carrier material, for example, aluminum oxide, aluminum oxide/silicon oxide, either alone or in a mixture, such as, for example, magnesium oxide, titanium oxide, etc. These carrier materials can comprise fibrous tones, for example, sepiolite, halloysite, imogolite, or attapulgite, in general with an inorganic oxide bonding agent. In dependence upon the application, the base can also contain aluminum silicates such as zeolite, etc. Suitable carrier compositions and processes for their production are known to the experts and are described, for example, in the above-named patent publications.

The catalyzer particles contain generally also catalytic metals, in particular elements of the group VIa of the periodic system such as molybdenum and tungsten (corresponding to group VIb in the Anglo-saxon literature) and group VIII of the periodic system, such as cobalt and nickel.

/15

The catalytic metals are typically present in a range of between 2 and 30 wt.-%, preferably between 5 to 15 wt.-%, for the elements of group VIa and between 0 and 10 wt.-%, preferably 2 to 6 wt.-% for the elements of group VIII, where the percentile proportions are based on the reduced metal divided by the catalyzer weight. These catalytic metals are available usually in the form of metals, oxides, or preferably sulfides. The

selection of the proportion of catalytic metals depends from the catalytic base and the catalytic carrier material and the function which the catalyzer should carry out. These metals can be added to the particles according to any desired technique, for example, by congelation with the catalyzer base solution, mixing with base or carrier material solids, or impregnation of either the catalyzer base solids or the extruded catalyzer base or carrier material.

Even though the techniques for catalyzer production are known in the technical field, an example which is only meant for clarification is described herein, which should not limit the invention in any way. 8 ml 88% formic acid (specific weight 1.2) were added to 300 ml distilled water. This solution was added while mixing to 500 g Kaiser aluminum oxide or Kaiser alumina at approximately 50°C and approximately 50 ml/min. The mixing procedure was continued for a total of 20 minutes after adding the solution. A second solution of 6 ml 58% ammonium hydroxide, 200 ml distilled water, and 45 ml molybdenum solution (which was prepared in that 17.4 g molybdenum trioxide was dissolved in 17.2 ml 30% ammonium hydroxide and 26 ml distilled water) was added at approximately 60-65°C at 50 ml/min during the stirring procedure. The dough-like mixture was directly stretched through a mold of a shape according to the invention and dried on a sieve plate at 120°C for 2 hours and then at 200°C for 2 hours. The dried

extrudate was calcined at 680°C in water vapor for 1 hour and dry air for 30 min. /16

The catalyzer particles according to the invention possess a high crush strength or resistance to crush, in particular in comparison with other catalyzers, which contain holes to increase their surface/volume ratio, as can be seen in the table, which shows the crush strength of flat plates (flat plate crush strengths) of different catalyzer shapes and materials.

Table

Flat Plate Crush Strength (Kg/mm)

Shape	Ring	"Vehicle Wheel"	Hollow Oval Parallel to D.	Parallel to W.
Material				
Aluminum oxide	0.14	0.59	6.14	1.36
Fiber ton	0.64	1.95	6.05	1.91
Macroporous alumina (aluminum oxide)	<0.05	0.09	0.91	0.18

One can see that the abrasion or resistance to friction of the catalyzer material particles is influenced by their pressure or crush strength; a better resistance generally goes together with a higher strength.

The particles also possess a high integrity, in particular when the pressure force is applied vertical to the line which connects

the two centers of the holes as expected in the packed bedding. The cross section of the particles does not change until the pressure or crush force is applied which is necessary to pulverize the particles. In contrast to the Kleeblatt catalyzers shown in United States patent 3,674,680 in which the arms can break the crush strengths which lie considerably below the crush strength necessary for pulverizing the particles, the catalyzers according to the invention retain their high particle integrity.

Applications

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The catalyzer particles according to the invention are particularly useful in hydroprocessing or hydrotreating (as defined above) and in particular in the hydroprocessing of heavy oil fractions such as residue and similar diffusion-limited reactions.

A typical hydroprocessing in which the catalyzers can be used comprises the flow of petroleum raw products through one or several catalyzer beddings in the presence of hydrogen gas. The beddings can contain catalyzers with different desired compositions. Typical compositions for the residue or residual hydroprocessing comprise an hourly liquid spacial speed of approximately 0.05 to 25, preferably 0.5 to 5 per hour; a temperature between 200 and 500°C, preferably between 350 and

450°C; a pressure between 1.4 to 70 mPa, preferably between 4 and 20 mPa, wherein at least 60%, preferably at least 80% of the pressure is supplied by the hydrogen; as well as a hydrogen/raw matter ratio of 90 to 900 Norm L/L, preferably 350 to 750 L/L. The catalyzer is useful as protective bedding or monitoring bedding catalyzer due to its resistance against intermediate space blocking.

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Nummer:

Int. Cl.4:

Anmeldetag:

Offenlegungstag:

35 39 195

B 01 J 35/02

5. November 1985

7. Mai 1986

FIG. 1.

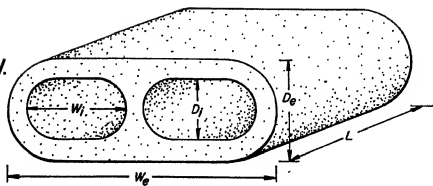


FIG. 2.

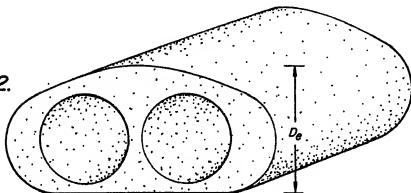


FIG. 3.

